(19) Europäisches Patentamt
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(11) EP 2 505 607 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
03.10.2012 Bulletin 2012/40

(21) Application number: **12001996.3**

(22) Date of filing: **21.03.2012**

(51) Int Cl.:
C08L 25/12 *(2006.01)*
C08K 5/523 *(2006.01)*
C08L 75/04 *(2006.01)*
C08L 55/02 *(2006.01)*
C08L 63/00 *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **01.04.2011 KR 20110030007**

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(54) Thermoplastic ABS resin compositions having excellent resistance to flame retardancy

(57) Disclosed is a thermoplastic flame retardant ABS resin composition. More specifically, disclosed is a thermoplastic flame-retardant resin composition containing: (A) 100 parts by weight of a base resin consisting of 10 to 90% by weight of an acrylonitrile-butadiene-styrene copolymer and 90 to 10% by weight of a styrene-acrylonitrile copolymer; (B) 1 to 30 parts by weight of an epoxy resin, and (C) 1 to 30 parts by weight of a phosphorous-based flame retardant.

Advantageously, the flame retardant resin composition exhibits superior flame retardancy to external candle flame ignition.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a thermoplastic and flame retardant ABS resin composition. More particularly, the present invention relates to a thermoplastic and flame retardant ABS resin composition with superior flame retardancy to external candle flame ignition.

Description of the Related Art

[0002] In general, an acrylonitrile-butadiene-styrene (hereinafter, referred to as ABS) resin is widely used as exterior materials of electric/electrical products and office machines and the like due to stiffness and chemical resistance of acrylonitrile, and processability and mechanical properties of butadiene and styrene. However, the ABS resin is inherently readily combustible and exhibits extremely poor flame retardancy.

[0003] Due to these problems, the ABS resin used for electric/electrical products, office machines and the like should satisfy flame-retardancy standards in order to secure safety to flames.

[0004] Methods for imparting flame retardancy to ABS resins include polymerization of rubber-modified styrene resins through incorporation of flame-retardant monomers, mixing flame retardant and auxiliary flame retardants with the prepared rubber-modified styrene resins and the like. Examples of the flame retardants include halogen flame retardants, non-halogen flame retardants such as phosphorous, nitrogen and hydroxide flame retardants, and examples of the auxiliary flame retardants include antimony compounds, silicon compounds, zinc compounds and the like.

[0005] The halogen flame retardants exhibit high flame retardancy efficiency, as compared to non-halogen flame retardants, and exhibit superior mechanical properties comparable to rubber-modified styrene resins. For this reason, imparting flame retardancy to ABS resins using halogen flame retardants is currently the most generally used method. Of these, bromine-based flame retardants are particularly efficient. However, when a bromine-based flame retardant is incorporated during processing of ABS resins, thermal stability is deteriorated and the flame retardant is decomposed due to high temperatures and pressures during the processing, thus causing generation of corrosive toxic gases and negatively affecting work environments and human health. This is a problem which also occurs when the ABS resin processed by incorporating a bromine-based flame retardant combusts.

[0006] In an attempt to avoid these problems, a non-halogen flame retardant is used and, in particular, a phosphorous-based flame retardant is generally used. However, phosphorous-based flame retardants are disadvantageously incorporated in an excessive amount due to low flame retardant efficiency, as compared to halogen flame retardants. In addition, thermoplastic resin compositions which do not generate char cannot sufficiently exert flame retardancy due to the principle of phosphorous-based flame retardant systems.

[0007] Meanwhile, there is a vertical combustion test method in accordance with UL94 as a flame retardant standard and a flame retardancy identification test method. This method is a standard to evaluate flame resistance against inner combustion caused by short circuit or the like of a circuit substrate present in a final electric product. Meanwhile, an external candle flame ignition standard (related standard: IEC TS 62441) which is standardized is a standard through which flame resistance of a final product is evaluated, when a candle as an exterior ignition source comes in contact with the product due to changes in outer environments such as earthquakes.

[0008] The external candle flame ignition standard is utilized in a wider range of applications since subjects to which the standard is applied are all combustible materials and is more realistic since the standard presumes a case of flames of burning candles as fires which may be often generated in houses.

SUMMARY OF THE INVENTION

[0009] In an attempt to solve these problems, the inventors of the present invention discovered that flame retardancy to external candle flame ignition can be obtained by incorporating a phosphorous-based flame retardant and an epoxy resin as a char-generating material into a thermoplastic resin comprising an acrylonitrile-butadiene-styrene copolymer and a styrene-acrylonitrile copolymer. The present invention has been completed based on this discovery.

[0010] Therefore, the present invention has been made in view of the above problems, and it is an object of the present invention to provide a resin composition with superior flame retardancy to external candle flame ignition.

[0011] In accordance with an aspect of the present invention, the above and other objects can be accomplished by the provision of a thermoplastic flame-retardant resin composition comprising: (A) 100 parts by weight of a base resin consisting of 10 to 90% by weight of an acrylonitrile-butadiene-styrene copolymer and 90 to 10% by weight of a styrene-acrylonitrile (hereinafter, referred to as SAN) copolymer; (B) 1 to 30 parts by weight of an epoxy resin; and (C) 1 to 30

parts by weight of a phosphorous-based flame retardant.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Hereinafter, the present invention will be described in detail.

[0013] The thermoplastic flame-retardant resin composition of the present invention comprises (A) 100 parts by weight of a base resin consisting of 10 to 90% by weight of an acrylonitrile-butadiene-styrene copolymer and 90 to 10% by weight of a styrene-acrylonitrile copolymer, (B) 1 to 30 parts by weight of an epoxy resin, and (C) 1 to 30 parts by weight of a phosphorous-based flame retardant.

[0014] The acrylonitrile-butadiene-styrene copolymer can be prepared in the form of a powder by subjecting a butadiene rubber, an acrylonitrile monomer and a styrene monomer to emulsion graft polymerization, followed by aggregation, dehydration and drying, but is not particularly limited thereto. Preferably, a butadiene rubber having an average particle size of 0.1 to 0.5 μm is present in a high percentage by weight.

[0015] Emulsion graft polymerization is preferably carried out by continuously or simultaneously incorporating a monomer mixture consisting of 5 to 40 parts by weight of acrylonitrile and 20 to 65 parts by weight of styrene into a mixed solution consisting of 50 to 70 parts by weight of butadiene rubber, 0.6 to 2 parts by weight of an emulsifying agent, 0.2 to 1 parts by weight of a molecular weight modifier, and 0.05 to 0.5 parts by weight of a polymerization initiator, based on 100 parts by weight of the total content of the monomers present in the acrylonitrile-butadiene-styrene copolymer.

[0016] Aggregation is preferably carried out in the presence of a 5% aqueous sulfuric acid solution.

[0017] The styrene-acrylonitrile copolymer has a weight average molecular weight of 50,000 to 150,000 and contains 20 to 40% by weight of an acrylonitrile monomer, and may be used alone or in combination of two or more types.

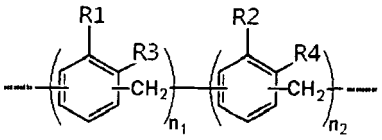
[0018] In terms of mechanical properties of resins, preferably, the ABS copolymer constituting a base resin is present in an amount of 10 to 90% by weight and SAN is present in an amount lower than 90 to 10% by weight and, more preferably, the ABS copolymer is present in an amount of 10 to 50% by weight and SAN is present in an amount of 90 to 50% by weight.

[0019] Any epoxy resin may be used without any particular limitation so long as it is miscible with the base resin and generates char when a processed thermoplastic resin combusts.

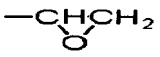
[0020] Preferably, the epoxy resin is selected from a urethane-modified epoxy resin represented by the following Formula 1, a multifuntional epoxy resin represented by the following Formula 3, an epoxy derivative represented by the following Formula 4, and a combination thereof, in terms of improvement of external candle flame ignition flame retardancy.

[0021] Of these, the urethane-modified epoxy resin is obtained by addition-reacting a compound having a urethane functional group with an epoxy ring and has a structure in which urethane-modified epoxy groups and non-urethane-modified epoxy groups are present as a mixture in one molecule.

[Formula 1]



wherein R1 is an epoxy group having a structure of

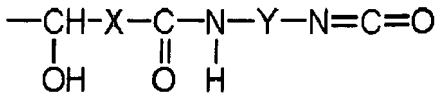


,

R3 and R4 are independently a hydrogen atom or an alkyl group having 1 to 20 carbon atoms or an aryl group, and n1 and n2 are natural numbers of 1 to 100,

R2 is a group represented by Formula 2 in which a terminal thereof is substituted by an isocyanate group.

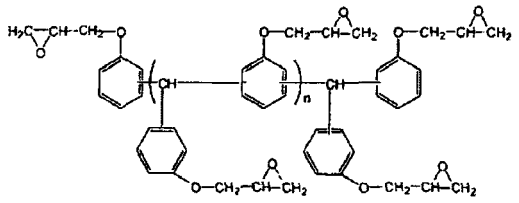
[Formula 2]



wherein X and Y are an alkyl group having 1 to 20 carbon atoms or an aryl group, each of which optionally contains oxygen, nitrogen or the like.

[0022] The multifuntional epoxy resin may be represented by the following Formula 3:

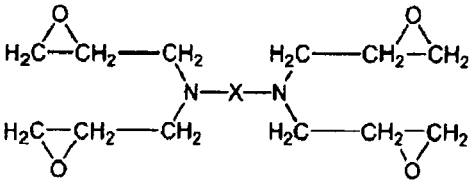
[Formula 3]



wherein n is a natural number of 1 to 100.

[0023] The epoxy derivative may be represented by the following Formula 4:

[Formula 4]



wherein X is alkyl having 1 to 30 carbon atoms or an aryl group, in which X optionally contains oxygen, nitrogen or the like.

[0024] The urethane-modified epoxy resin, multifuntional epoxy resin, or epoxy derivative constituting the epoxy resin may be used alone or in combination of two or more types.

[0025] Preferably, the epoxy resin is present in an amount of 1 to 30 parts by weight, based on 100 parts by weight of the base resin. The reason behind this is that the thermoplastic resin composition prepared within this range produces char and thus exhibits superior flame retardancy without using an excess of phosphorous-based flame retardant.

[0026] Preferably, the phosphorous-based flame retardant is present in an amount of 1 to 30 parts by weight, based on 100 parts by weight of the base resin. The thermoplastic resin composition prepared within this range is effective in exhibiting superior flowability or gloss without greatly causing deterioration in mechanical properties or thermal stability.

[0027] Any phosphorous-based flame retardant may be used without particular limitation so long as it is commonly used for thermoplastic resins. Examples of the phosphorous-based flame retardant include organic phosphorous-based flame retardants such as phosphate compounds including triphenylphosphate, tricresylphosphate, tri(2,6-dimethylphenyl)phosphate, and tri(2,4,6-trimethylphenyl)phosphate, diphosphate compounds including tetraphenyl resorcinol diphosphate, tetracresyl resorcinol diphosphate, tetra(2,6-dimethylphenyl)resorcinol diphosphate, tetraphenyl bisphenol A diphosphate, polyphosphate compounds having three or more phosphate groups, phosphonate compounds, and phosphinate compounds. This compound may be used alone or combinations thereof.

[0028] The method for preparing the thermoplastic flame retardant resin composition with superior flame retardancy according to the present invention may comprise adding the components A) to C) to an extruder, and mixing and extruding the same at a barrel temperature of 230 to 250°C. The extruder is not particularly limited and may be a twin screw extruder.

[0029] Now, the present invention will be described in more detail with reference to the following Examples. These examples are only provided to illustrate the present invention and should not be construed as limiting the scope and spirit of the present invention.

[Example 1]

[0030] 10 parts by weight of a urethane-modified epoxy resin of Formula 1 (product name: KD-1090, available from

Kukdo Chemical Co., Ltd.) as an epoxy resin, and 10 parts by weight of tetra(2,6-dimethylphenyl)resorcinol diphosphate (product name: PX-200, available from Daihachi Kagaku Kogyo Co., Ltd., Japan) as a phosphorous-based flame retardant were added to 100 parts by weight of a base resin consisting of 25 parts by weight of an ABS copolymer (containing 55% by weight of a butadiene rubber) produced by LG Chem. Ltd. from a butadiene rubber latex having an average particle size of 0.3 μm by emulsion graft polymerization and 75 parts by weight of a styrene-acrylonitrile copolymer containing 25% by weight of acrylonitrile and having a weight average molecular weight of 120,000, the resulting mixture was homogeneously mixed using a Hansel mixer and a thermoplastic resin composition was prepared in the form of a pellet through a twin screw extruder.

[0031] The pellet-form thermoplastic resin composition was subjected to injection molding to produce samples for flame retardancy testing having a width of 10 centimeters, a length of 10 centimeters and a thickness 3 millimeters.

[Example 2]

[0032] The same test as in Example 1 was repeated except that a multifuntional epoxy resin of Formula 3 (product name: DNTH, available from Nippon Kayaku Co., Ltd.) was used as an epoxy resin instead of the urethane-modified epoxy resin of Formula 1.

[Example 3]

[0033] The same test as in Example 1 was repeated except that a multifuntional epoxy resin of Formula 4 (product name: KDT-4400, available from Kukdo Chemical. Co., Ltd.) was used as an epoxy resin instead of the urethane-modified epoxy resin of Formula 1.

[Example 4]

[0034] The same test as in Example 1 was repeated except that 8 parts by weight of a urethane-modified epoxy resin of Formula 1, 1 part by weight of a multifuntional epoxy resin of Formula 3 and 1 part by weight of an epoxy derivative of Formula 4 were added as epoxy resins.

[Comparative Example 1]

[0035] The same test as in Example 1 was repeated except that neither phosphorous-based flame retardant nor epoxy resin was added.

[Comparative Example 2]

[0036] The same test as in Example 1 was repeated except that 20 parts by weight of a urethane-modified epoxy resin was added as an epoxy resin and a phosphorous-based flame retardant was not added.

[Comparative Example 3]

[0037] The same test as in Example 1 was repeated except that 20 parts by weight of a multifuntional epoxy resin was added as an epoxy resin and a phosphorous-based flame retardant was not added.

[Comparative Example 4]

[0038] The same test as in Example 1 was repeated except that 20 parts by weight of an epoxy derivative was added as an epoxy resin and a phosphorous-based flame retardant was not added.

[Comparative Example 5]

[0039] The same test as in Example 1 was repeated except that an epoxy resin was not added and 20 parts by weight of a phosphorous-based flame retardant was added.

[Comparative Example 6]

[0040] The same test as in Example 1 was repeated except that 10 parts by weight of an o-cresol novolac epoxy resin was added as an epoxy resin and 10 parts by weight of a phosphorous-based flame retardant was added.

[Experimental Example]

[0041] The external candle flame ignition flame retardancy of thermoplastic flame-retardant resin composition samples prepared in Examples 1 to 4 and Comparative Examples 1 to 6 were measured in accordance with IEC TS 62441 and the results thus obtained are shown in Table 1 below. A case wherein the flame source was removed and flames flared on flame-retardant resin composition samples were then extinguished within 3 minutes in accordance with the standard, was represented by "PASS" and, otherwise, were represented by "FAIL".

[TABLE 1]

Items		Examples				Comparative Examples					
		1	2	3	4	1	2	3	4	5	6
Emulsion-polymerized ABS		25	25	25	25	25	25	25	25	25	25
SAN		75	75	75	75	75	75	75	75	75	75
Epoxy resin	Urethane-modified epoxy resin	10	-	-	8	-	20	-	-	-	-
	Multifuntional epoxy resin	-	10	-	1	-	-	20	-	-	-
	Epoxy derivative	-	-	10	1	-	-	-	20	-	-
	o-cresol novolac epoxy resin	-	-	-	-	-	-	-	-	-	10
Phosphorous-based flame retardant		10	10	10	10	-	-	-	-	20	10
Test results of external candle flame ignition		PASS	PASS	PASS	PASS	FAIL	FAIL	FAI L	FAIL	FAI L	FAIL

[0042] As can be seen from Table 1 above, Examples 1, 2, 3 and 4 in which both the epoxy resin and the phosphorous-based flame retardant were incorporated passed the flame retardancy standard of external candle flame ignition.

[0043] On the other hand, it can be seen that Comparative Example 1 in which neither epoxy resin nor phosphorous-based flame retardant was incorporated, and Comparative Example 2, 3, 4 and 5 in which either an epoxy resin or a phosphorous-based flame retardant was incorporated did not pass the external candle flame ignition standard.

[0044] In particular, flame retardant samples of Comparative Examples 1, 2, 3 and 4 were completely destroyed by fire since they did not contain a phosphorous-based flame retardant, and the sample of Comparative Example 5 was slightly ignited owing to the effect of phosphorous-based flame retardant, but was holed due to non-generation of char and underwent delayed extinguishment or was completely destroyed by fire.

[0045] In addition, it can be seen that the sample of Comparative Example 6 had a similar epoxy content to Examples 1, 2 and 3, but was completely destroyed by fire when combusted and could not pass the external candle flame ignition standard.

[0046] The o-cresol novolac epoxy resin used as an epoxy resin in Comparative Example 6 was considered to be a compound having low char production effects, which corresponds to a starting material prior to preparation of a urethane-modified epoxy (n2 in Formula 1 is 0) as a urethane-modified epoxy resin of Formula 1 in which the epoxy group was not substituted at all and the epoxy group still remained.

[0047] In conclusion, the thermoplastic resin composition of the present invention satisfies flame retardancy standards of external candle flame ignition based on production of char using both an epoxy resin and a phosphorous-based flame retardant.

[0048] As apparent from the above description, the present invention provides a thermoplastic resin composition with superior flame retardancy containing both an epoxy resin and a phosphorous-based flame retardant. In particular, the composition can satisfy flame retardancy identification standard, external candle flame ignition identification.

[0049] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing

from the scope and spirit of the invention as disclosed in the accompanying claims.

Claims

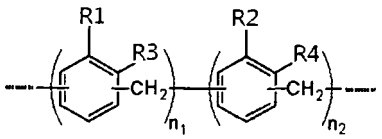
1. A thermoplastic flame-retardant resin composition comprising:

   (A) 100 parts by weight of a base resin consisting of 10 to 90% by weight of an acrylonitrile-butadiene-styrene copolymer and 90 to 10% by weight of a styrene-acrylonitrile copolymer;
   (B) 1 to 30 parts by weight of an epoxy resin; and
   (C) 1 to 30 parts by weight of a phosphorous-based flame retardant.

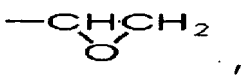
2. The thermoplastic flame-retardant resin composition according to claim 1, wherein the (B) epoxy resin is selected from the group consisting of a urethane-modified epoxy resin, a multifuntional epoxy resin, an epoxy derivative and a combination thereof.

3. The thermoplastic flame-retardant resin composition according to claim 2, wherein the urethane-modified epoxy resin satisfies Formula 1 below:

[Formula 1]

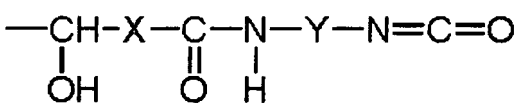


wherein R1 is an epoxy group having a structure of



R3 and R4 are independently a hydrogen atom or an alkyl group having 1 to 20 carbon atoms or an aryl group, and n1 and n2 are natural numbers of 1 to 100,
R2 is a group represented by Formula 2 in which a terminal thereof is substituted by an isocyanate group.

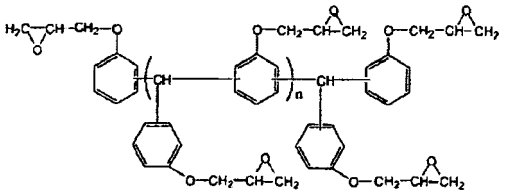
[Formula 2]



wherein X and Y are an alkyl group having 1 to 20 carbon atoms or an aryl group, each of which optionally contains oxygen or nitrogen.

4. The thermoplastic flame-retardant resin composition according to claim 2, wherein the multifuntional epoxy resin satisfies Formula 3 below:

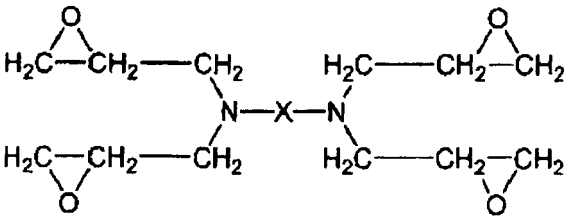
[Formula 3]



wherein n is a natural number of 1 to 100.

5. The thermoplastic flame-retardant resin composition according to claim 2, wherein the multifuntional epoxy resin satisfies Formula 4 below:

[Formula 4]



wherein X is alkyl having 1 to 30 carbon atoms or an aryl group, in which X optionally contains oxygen or nitrogen.

6. The thermoplastic flame-retardant resin composition according to claim 1, wherein the acrylonitrile-butadiene-styrene copolymer contains 50 to 70% by weight of a butadiene rubber and is prepared by emulsion graft polymerization.

7. The thermoplastic flame-retardant resin composition according to claim 1, wherein the styrene-acrylonitrile copolymer has a weight average molecular weight of 50,000 to 150,000, and contains 20 to 40% by weight of an acrylonitrile monomer.

8. The thermoplastic flame-retardant resin composition according to claim 1, wherein the (C) phosphorous-based flame retardant is selected from the group consisting of phosphate compounds, diphosphate compounds, polyphosphate compounds having three or more phosphate groups, phosphonate compounds, phosphinate compounds, and metal diethyl phosphinate compounds and combinations thereof.

9. The thermoplastic flame-retardant resin composition according to claim 1, wherein the resin composition further comprises one or more additives selected from the group consisting of an impact modifier, a heat stabilizer, an antidropping agent, an antioxidant, a photostabilizer, a UV blocker, a pigment and an inorganic filler and a combination thereof.

10. The thermoplastic flame-retardant resin composition according to claim 1, wherein the resin composition satisfies a flame retardancy standard of external candle flame ignition.

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EUROPEAN SEARCH REPORT

Application Number
EP 12 00 1996

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 312 644 A1 (TORAY INDUSTRIES [JP]) 21 May 2003 (2003-05-21) * claims; examples * -----	1-10	INV. C08L25/12 C08L55/02 C08K5/523 ADD. C08L63/00 C08L75/04
X	JP 2002 201330 A (TORAY INDUSTRIES) 19 July 2002 (2002-07-19) * Comparative examples 2, 7 and 8;claims; tables * -----	1-10	
X	LEE K ET AL: "Studies on the thermal stabilization enhancement of ABS; synergistic effect by triphenyl phosphate and epoxy resin mixtures", POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 43, no. 8, 1 April 2002 (2002-04-01), pages 2249-2253, XP004335727, ISSN: 0032-3861, DOI: 10.1016/S0032-3861(02)00024-1 * the whole document * -----	1-10	

TECHNICAL FIELDS SEARCHED (IPC)
C08L
C08K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	29 June 2012	Enrique de Los Arcos

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 12 00 1996

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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29-06-2012

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82